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Polymer 48 (2007) 4328–4336
polymer
www.elsevier.com/locate/polymer

Chemical stability of conducting polymers: Friedel–Crafts reactions of alcohols with poly(3,4-ethylenedioxythiophene) (PEDOT)

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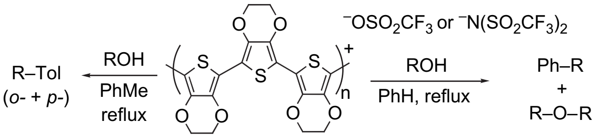
Received 27 February 2007; received in revised form 14 May 2007; accepted 19 May 2007
Available online 25 May 2007

Abstract

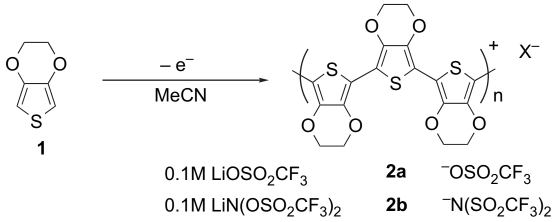


The conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) facilitates a Friedel–Crafts reaction between benzylic or allylic alcohols and benzene or toluene, giving the arene and water as a by-product. Aliphatic alcohols gave poorer yields of coupling product, and elimination to the corresponding alkene is a competitive process in many cases. The results are consistent with an acid-catalyzed Friedel–Crafts reaction, although we have not determined the mechanism with respect to the polymer as yet. However, it is clear that PEDOT facilitates this reaction, and the formation of water as a by-product may have implications in its commercial applications.

Keywords: Poly(ethylenedioxy)thiophene; Conducting polymer; Friedel–Crafts alkylation

1. Introduction

We have observed that the conducting polymer poly(ethylenedioxythiophene) [**2**], facilitates the reaction of alcohols with benzene or toluene, to form Friedel–Crafts alkylation products without the need to attach reactive components to the polymer [1]. The by-product of this reaction is water. The observed coupling reaction is heterogeneous, as **2** is insoluble in the solvents used. The Friedel–Crafts products are readily removed from the polymer by simple filtration, and we have used **2** several times in subsequent reactions without further purification or other treatment, suggesting there is no significant change in the polymer itself.



In general, conducting polymers have been used as semiconductors for field-effect transistors [2] and LEDs [3], conductors for electrostatic charge dissipation and EMI

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doi:10.1016/j.polymer.2007.05.051

shielding, as redox active materials for energy storage (batteries and super-capacitors) and as electronic devices [4]. PEDOT in particular has seen use in anti-static coatings [5], in solid electric capacitors [6], electroluminescent devices [7], and underlayers for metalization of printed circuit boards [8]. The conductive properties of such polymers led us to raise the question of chemical reactivity, particularly with known additives that enhance conductivity. Chemical modification of the polymer itself is known and polymers bearing an acidic functional group that can induce chemical reactions are known (see below), but chemical reactions induced by PEDOT alone have not been reported. The commercial importance of PEDOT, along with the ease of preparation and handling, stability in air and solvents, and its conductive properties led us to choose **2** for our study. Pei synthesized the requisite monomer (3,4-ethylenedioxythiophene, EDOT, **1**), beginning with commercially available thiodiglycolic acid [9], but EDOT is commercially available and known as Baytron-M [10].

For the most part, organic polymers are not viewed as chemical reagents. Organic polymers are known to be electrical insulators, and offer the advantages of ease of fabrication, flexibility or strength, light weight, but in most applications are considered to be chemically inert [11]. Chemical reactions at the polymer itself are well-known. Overoxidation of poly (3-methylthiophene) in the presence of chloride or bromide led to substitution of the hydrogen at the 4-position by the halide [12]. Under electrochemical overoxidation conditions (+1.40 V) in acetonitrile and tetraethylammonium perchlorate containing 10% methanol, poly(3-methylthiophene), the thiophene unit reacted with 3-bromopropanol to form the 4-substituted ether [13]. Similar reaction of water via electrochemical oxidation of poly(thiophenes) and poly(pyrroles) is also known [14]. Post-functionalization of conjugated polymers in this manner has been well-studied [14,15], and the reaction of poly(3-alkylthiophenes) with NBS or NCS and then fuming nitric acid gave functionalized polymers [16]. Polyaniline can also be chemically modified [17], and the reaction of polyaniline with substituted benzenediazonium ions has been reported [18]. Poly(pyrrole-*N*-propanoic acid) esters have been shown to react with nucleophiles such as amines to produce the corresponding amide [19]. Conducting poly(thiophenes) have been developed that contain nucleophilic groups, used for immobilizing biomolecules, but this nucleophilic chemistry does not occur in polymers that have not been modified to contain these groups [20].

Polymers that are known to induce reactions in other molecules are those with acidic properties such as Nafion [21], and there are many reactions catalyzed by ion-exchange resins [22], including the industrial synthesis of methyl *tert*-butyl ether (MTBE) with a polymer-bound acid catalyst [23]. Many polymers contain reactive functionality (a reactive unit is bound to or coordinated with the polymer), and such polymers have been used as chemical reagents to induce reactions in other molecules for a variety of transformations [24]. Ley described the use of polymer-bound reagents in fine organic synthesis [25]. Polymer-bound reagents are extensively used in combinatorial chemistry, where libraries of targeted compounds are produced [26], and polymer-bound reagents form the basis of the Merrifield synthesis of peptides, which is probably the first example that uses this approach [27].

In our work, PEDOT induces chemical reactions of alcohols without overoxidation, without incorporating reactive functional groups, and without adding additional reagents. PEDOT is a polycation, but the literature contains no report of ether formation or Friedel–Crafts alkylation in the presence of PEDOT, despite the use of alcohols as additives. Alcohol additives can modify the morphology and electronic characteristics of the polymer [28]. Electrical conductance is increased in cast PEDOT–PSS films by blending the PEDOT–PSS dispersion with a mixture of sorbitol, *N*-methylpyrrolidone and isopropanol [29]. It has been suggested that this effect is due to the solvent acting as a secondary dopant or lubricant, providing better mixing of PEDOT and PSS, elongating the PEDOT–PSS coils, and increasing π-conjugation [30]. This enhancement in conductivity has also been explained by an increase in PEDOT content at the surface of the film, thus at the grain boundaries [31]. Electro-oxidation of alcohols using electrodes modified with PEDOT and platinum particles [32], or other metals [33] has been reported. In these latter results, the alcohol reacts with the metal, which is dispersed on the polymer. There is no claim than PEDOT facilitates a chemical reaction.

Our results show that **2** facilitates a Friedel–Crafts alkylation reaction with alcohols, and water is produced as a by-product. This observation raises the issue of whether or not water may be formed during the operation of commercial applications that use PEDOT. Since alcohols are common additives and PEDOT contains the aromatic thiophene unit, the question concerning possible reactivity in applications using PEDOT is reasonable.

To begin this study, we electropolymerized two variants of PEDOT for this study, from ethylenedioxythiophene (EDOT, **1**), by procedures reported in the literature. Electrochemically prepared PEDOT **2a** [34], from a 40 mM EDOT solution in 0.1 M lithium triflate solution in acetonitrile, was removed from the electrode, washed with solvent, dried *in vacuo*, and used directly in subsequent reactions. We prepared the related electrochemically generated polymer **2b**, using lithium triflimide as an electrolyte [35]. The resulting polymer was removed from the electrode, washed, dried, and used directly in subsequent reactions. For the electrochemically generated **2**, the unit structure used for the stoichiometric calculation in chemical reactions was a trimeric mono-cation with a triflate or triflimide counterion (**2a** and **2b**) [34,35]. The doping level in **2a** and in **2b** was confirmed using the electrochemical quartz crystal microbalance (EQCM). The active form of this polymer is normally described as a combination of polarons and bipolarons (single and paired positive charges) [36].

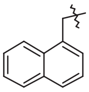
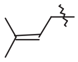
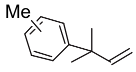
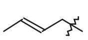
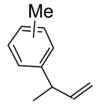
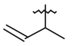
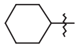
As mentioned above, refluxing benzyl alcohol with PEDOT (in hexane) gave dibenzyl ether in greater than 80% yield, along with small amounts of benzaldehyde [1a]. Refluxing benzyl alcohol in benzene did not give the ether, but rather the Friedel–Crafts alkylation product [37] diphenylmethane, in about 32% yield. Alcohols are known substrates for the Friedel–Crafts alkylation reaction, but a protonic acid or a good Lewis acid is required, and sulfuric acid is the most common catalyst. Further, it is known that alcohols react with sulfuric acid to form an alkyl sulfate that subsequently reacts with the aromatic compound [38], and there is nothing in the literature to suggest that PEDOT without PSS and without an acidic functional group possesses this type of acid property. When Lewis acids are used to facilitate the reaction of aromatic compounds and alcohols, large quantities of a Lewis acid are usually required [39]. Alcohols are prone to side reactions with Lewis acids, as in the complex formed when alcohols react with aluminum chloride, with formation of an alkyl chloride [40], and a full equivalent of the Lewis acid is required to form this complex. The cation-radical nature of PEDOT can lead to speculation that there is a potential for behavior as a Lewis acid, but the literature does not provide evidence for this assumption. In one experiment, we refluxed benzyl chloride in benzene, in the presence of PEDOT, but no reaction occurred. If the PEDOT functions as a Lewis acid, it only does so in the presence of the alcohol. Although our results clearly point to an acid-catalyzed reaction, the method of preparation of the polymer, and the reaction itself do not point to the presence of an endogenous acid. The mechanism of this process is not straightforward, and we are currently examining various mechanistic possibilities.

$$\begin{matrix}\text{R—Tol}\\(o\text{- + }p\text{-})\end{matrix}\ \xleftarrow[\text{PhMe reflux}]{\text{ROH}}\ \begin{matrix}\mathbf{2a}\\\mathbf{2b}\end{matrix}\ \xrightarrow[\text{PhH , reflux}]{\text{ROH}}\ \begin{matrix}\text{Ph—R}\\+\\\text{R—O—R}\end{matrix}$$

We chose to examine the scope of this reaction in a limited way, in part to confirm the reactivity with other aromatic compounds and other alcohols. We examined three different classes of alcohols: benzylic, allylic, and aliphatic. In all, 10 alcohols were examined in this study with **2a**, in both toluene and benzene. We used the trimeric structure of **2a** as the stoichiometric unit of the polymer, in reaction with one equivalent of the appropriate alcohol. The benzylic alcohols were the most reactive, and toluene was more reactive in Friedel–Crafts coupling than benzene, as expected. In most cases, only the Friedel–Crafts products, unreacted alcohol or ether were observed in toluene. There was no evidence of polymer decomposition in any reaction, suggesting that formation of by-products are not responsible for the observed reactivity.

As shown in Table 1, benzylic alcohols gave the best yield of Friedel–Crafts alkylation. The Friedel–Crafts alkylation was much faster in toluene than in benzene, where formation of the homo-ether was a competitive process in some cases. The reaction of benzyl alcohol in toluene, for example, gave >98% of *o*- and *p*-benzyltoluene, and we observed <2% of the *meta*-product, which was typical in all cases. Allylic alcohols gave virtually no coupling product in benzene despite the loss of starting material, although reaction in toluene was straightforward in most cases. Decomposition of the alcohol, elimination, or polymerization are possible processes in benzene, although we were unable to isolate products from the allylic alcohols that would prove any of these pathways.

Table 1
Coupling products of alcohols with benzene and toluene mediated by **2a**

ROH	R–Ph	MeC_6H_4R $(o+p)$[a]
$PhCH_2$	32%[b]	>98%
Ph_2CH	47%[c]	93%
$PhCH{=}CH{-}CH_2$	[d]	67%
	Quant	77%
	<5%	 quant
	<5%	 quant
	<5%	<5%
	[e]	[f]
$C_7H_{15}CH_2$	[g]	[g]
$C_6H_{13}(Me)CH$	[g]	[g]

[a] <2% of *meta*-coupling product observed in all cases.

[b] Recovered 40% of benzyl alcohol + 28% dibenzyl ether.

[c] +53% yield of $Ph_2CHOCHPh_2$.

[d] Loss of alcohol with formation of unidentifiable products. No ether or coupling products.

[e] Recovered 74% of unreacted cyclohexanol, along with 26% of dibromocyclohexane by adding bromine to the filtered hexane solution.

[f] No alcohol recovered. Small amount of dibromide obtained by adding bromine to filtered hexane solution.

[g] Little or no reaction, with recovered alcohol. Trace amounts of what appears to be alkene by GC/MS analysis.

Aliphatic alcohols gave some elimination along with trace amounts of Friedel–Crafts products. Cyclohexanol, for example, showed complete loss of starting material in toluene, but no Friedel–Crafts coupling or ether formation. In benzene, we recovered only 74% of the alcohol. We suspected elimination, and after the initial reaction in refluxing toluene, **2a** was filtered off and elemental bromine was added to the reaction mixture. After stirring the resulting solution overnight, protected from light, GC/MS analysis showed the presence of 1,2-dibromocyclohexane in the toluene reaction. We isolated 26% of 1,2-dibromocyclohexane from a similar reaction in refluxing benzene, after chromatography on silica gel. This experiment confirmed the generation of the elimination product cyclohexene, although we could not verify the extent of this conversion. As with Friedel–Crafts coupling, the by-product of the elimination reaction is water. The secondary alcohol cyclohexanol showed a much greater propensity for elimination when compared to the reaction of 1-octanol or 2-octanol under identical conditions. Cyclohexanol did not give dicyclohexyl ether as a product. 1-Octanol and 2-octanol were particularly unreactive, although in toluene, there were indications that a small amount of ether formed in the case of the former alcohol.

We were interested in the polymer itself, since the PEDOT appeared to be largely unchanged after the reaction with the alcohol. We used one batch of **2a** five times for the Friedel–Crafts alkylation of benzyl alcohol in toluene, without an observable change in reactivity, or yield of products. In each experiment, **2a** was filtered, washed with toluene, dried under nitrogen, and added to a toluene/benzyl alcohol solution for the next reaction. We also examined the reaction using only "35%" of **2a** relative to benzyl alcohol, in toluene under the standard conditions (~0.017 M, reflux, overnight, N_2 atmosphere). The results were identical to those using one full equivalent of PEDOT, based on **2a**. When as little as 4% **2a** was used in the reaction with benzyl alcohol and toluene, we observed the same alkylation products. Some unreacted alcohol remained in the 4% reaction, in addition to <5% of an unidentified product. Obviously, this experiment raises some doubt concerning the stoichiometry of the polymer relative to the alcohol, as we have defined it, but the mechanism of this reaction has not been determined and the significance of this observation for possible catalytic activity is not yet clear. We observed no by-products such as thiophene derivatives or ether products derived from EDOT that pointed to polymer decomposition, and there was no significant change in the yield of the Friedel–Crafts products.

If these reactions are acid catalyzed, the source of the acid is unclear. We showed that refluxing lithium triflate with benzyl alcohol and toluene did *not* lead to Friedel–Crafts alkylation, but rather gave no reaction. Since **2a** was prepared from EDOT in acetonitrile by collection on an electrode, removed from the electrode, washed with dry acetonitrile and dried *in vacuo*, it seems unlikely that triflic acid is produced at this stage. The equilibrium of lithium triflate and triflic acid in acetonitrile clearly does not favor formation of triflic acid during the polymerization or the purification process. Indeed, triflic acid (trifluoromethanesulfonic acid) is one of the strongest known acids [41], and will even protonate sulfuric acid [41,42] Once **2a** is formed, one can ask if the triflate anion produces endogenous triflic acid, which would then be available to facilitate the reaction with added alcohols. In solvents such as hexane, benzene, or toluene, this is highly unlikely. It is known, for example, that in DMSO triflic acid is completely dissociated [43]. With the polar **2** in a non-polar solvent, we expect the polymer to contain only triflate and not triflic acid. The use of lithium triflate in polymers has been linked to formation of bidentate complexes, although the free triflate ion may also be present [44]. Although we cannot completely rule out the presence of endogenous triflic acid in **2b** formed by electropolymerization, its presence seems unlikely. Indeed, the presence of triflic acid observation would be an important observation for those using PEDOT.

An attempt to address these concerns led us to examine the ^{19}F NMR of the polymer in toluene, and we determined that there were no resonances that corresponded to triflic acid. In toluene, triflic acid showed a resonance at −47.60 ppm. When triflic acid was added to freshly prepared **2**, two resonances were observed in the ^{19}F NMR. One resonance at −47.74 ppm was close to that of the triflic acid (−47.60 ppm). The second resonance at −50.03 ppm is believed to be due to polymer-bound triflic acid. In fresh polymer that does not have added triflic acid, there is a small, broad signal that does not correlate with either of the triflic acid signals, and is likely due to the polymer counterion, the triflate anion. Our results confirm that there is less than 1% triflic acid in the polymer. The detection limits of NMR preclude us from ruling out its presence altogether, but we can certainly confirm that it is not detectable in these samples. We subjected the **2a** used once and the sample used up to five times to the same ^{19}F NMR procedure, and found that the NMR was identical to that of the unused **2a**. This finding is consistent with the conclusion that no triflic acid is present when **2a** is generated, or is retained on the polymer during the course of the reaction with alcohols.

Despite the encouraging evidence in the ^{19}F NMR, we examined the reaction of benzyl alcohol in the presence of added triflic acid, which would most certainly induce the Friedel–Crafts reaction. The results were somewhat different than those that were obtained with **2**. Specifically, when only 5 mol% of triflic acid was added, all of the benzyl alcohol was consumed with benzene as the reaction solvent. This result contrasts with the reaction of benzyl alcohol and **2** in benzene, where a significant amount of unreacted alcohol was observed along with dibenzyl ether. Further, when benzyl alcohol was refluxed with an equivalent of lithium triflate in toluene overnight, no reaction was observed, indicating that the triflate anion is not responsible for the observed reactivity, and no triflic acid is present in this medium. This result supports the premise that the equilibrium of triflic acid–lithium triflate does *not* favor formation of triflic acid.

We also prepared PEDOT with a triflimide counterion, bis(trifluoromethanesulfonyl) amide. As noted above, polymer **2b** was prepared in a manner identical to **2a**, but using lithium triflimide. The reaction of benzyl alcohol and **2b**, in refluxing toluene, gave results that were identical to those obtained with **2a**. In this experiment, the question is whether the highly acidic triflimide, $HN(SO_2CF_3)_2$ [$HNTf_2$] is present. The equilibrium of $^{-}NTf_2 \leftrightarrow HNTf_2$ strongly favors the anion, due the acidity of $HNTf_2$, which has been shown to be greater than that of triflic acid in the gas phase [45], although the acidity in liquid media need not follow this trend. We refluxed benzyl alcohol and one equivalent of $HNTf_2$ overnight in toluene, and isolated the Friedel–Crafts products 2- and 4-benzyltoluene in about 90% yield. We noted that triflimide fumes in air, which was not observed during the workup procedure of our reaction with benzyl alcohol. Although this experiment does not rule out the presence of $HNTf_2$, the reactivity profile and known chemistry of triflimide makes its presence is highly unlikely.

Our results are unequivocal, and show that alcohols react with benzene and toluene when heated in the presence of PEDOT **2**. The products of these reactions are consistent with an acid-catalyzed process, but all attempts to determine the source of the acid point away from endogenous acid, and to a complex between PEDOT and the alcohol that leads to reaction. This mechanistic suggestion is highly speculative at this point, since we do not have evidence to support a formal mechanism for the role of PEDOT. The mechanism with respect to the alcohol and aromatic compound, however, is unquestionably electrophilic aromatic substitution, consistent with an acid-catalyzed reaction, and the mechanistic role of PEDOT in this reaction is under investigation. Nonetheless, one thing is clear. *PEDOT reacts with alcohols in the presence of aromatic compounds to produce Friedel–Crafts alkylation products, and water.* Both water and air are painstakingly excluded from devices that use PEDOT. In PEDOT, there are likely oligomeric units that can have unsubstituted thiophene units. Alcohols are added to enhance conductivity in some cases, and alcohols are used in the fabrication of the conducting layers in other applications. Simply heating these layers and devices *in vacuo* will not dispel all traces of alcohols. If trace amounts of alcohol remain in a device, and if there are free thiophene units, Friedel–Crafts type reactions may be possible when heating occurs. If these water-producing reactions occur in the PEDOT layer of working devices, the results may be deleterious to the long-term operation of the device. We have begun a study to determine if this reaction occurs in working devices, based on our observations in this preliminary account.

2. Experimental

2.1. General

All solvents and chemicals were used as received. Unless otherwise indicated, all alcohols were purchased from Aldrich or Acros. An HP Model 5970B GC/MSD with an HP-1 column Gas chromatogram/mass spectrometer was used for all GC/MS spectra. ^{1}H and ^{13}C NMR were obtained on a Bruker Avance 300 (300.13 MHz ^{1}H; 75.48 MHz ^{13}C) or a Brüker DRX-400 (400.144 MHz ^{1}H; 100.65 MHz ^{13}C), and ^{19}F NMR were obtained on a Brüker DRX-400 (376 MHz). Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane. Due to the limited availability of **2a**, all reactions were run on 1 mmol scale, and unless otherwise noted, reported yields are crude.

2.1.1. Poly(3,4-ethylenedioxythiophene)

(3,4-Ethylenedioxy)thiophene (10 g, 70.3 mmol) was mixed with 0.1 M lithium triflate–acetonitrile solution (2 L). This solution was poured into the electrochemical cell containing two metal plates that acted as the working and counter electrodes, and an Ag/Ag+ reference electrode. Electropolymerization of EDOT was done at +1.3 V for 3000 s using chronoamperometry. The working electrode, coated with **2a**, was thoroughly washed with acetonitrile, and the **2a** was subsequently collected by scraping the electrode. The collected **2a** (3.5 g, 9%) was washed again with acetonitrile, dried under vacuum, and stored under nitrogen.

*2.1.1.2. Benzyl alcohol with **2a**. With benzene*: A 100 mL round-bottomed flask was charged with benzene (60 mL) and a magnetic stirbar. Benzyl alcohol (0.1 mL, 1 mmol) was added via syringe, and **2a** (0.57 g) was added in one portion. A reflux condenser equipped with a septum and N_2 inlet and outlet needles was attached. The mixture was stirred at reflux overnight. After cooling, the **2a** was removed by filtration through a fritted funnel, the polymer was washed with the reaction solvent and the mixture was analyzed by GC/MS and NMR, showing the presence of 40% benzyl alcohol, 28% dibenzyl ether, and 32% diphenylmethane. GC/MS For benzyl alcohol: 108 (M^+, 71), 91 (13), 79 (P^+, 100), and 51 (33). For dibenzyl ether: M^+ not observed, 107 (14), 92 (P^+, 100), 77 (21), and 65 (24). For diphenylmethane: GC/MS 168 (M^+, 93), 167 (P, 100%), 152 (23), 91 (19), 65 (13), and 51 (13). ^{1}H NMR (as a mixture) ($CDCl_3$): δ 1.96 (bs, 0.3H) 4.04 (s, 0.5H), 4.61 (s, 0.3H), 4.71 (s, 0.5H), and 7.23–7.42 ppm (m, 5H). ^{13}C NMR: δ 42.0, 65.4, 72.2, 126.1, 127.0, 127.7, 127.7, 127.9, 128.4, 128.5, 128.6, 129.0, 129.1, 138.3, 141.0, and 141.2 ppm.

In toluene: A 100 mL round-bottomed flask was charged with toluene (60 mL) and a stirbar. Benzyl alcohol (0.125 g, 1.15 mmol) was added via syringe, followed by **2a** (0.57 g). A condenser with a septum with N_2 inlet and outlet needles was attached. The mixture was refluxed overnight. After cooling, the **2a** was removed by filtration through a fritted funnel and the mother liquor was analyzed by GC/MS, evaporated and analyzed by NMR to show a mixture of *o*- and *p*-benzyltoluene, along with a trace amount of benzyl ether. Evaporation of the solvent gave an oil, and purification by column (silica gel, pentane) gave *o*- and *p*-benzyltoluene (0.2 g, >98%). GC/MS: 182 (M^+, 67), 167 (P^+, 100), 152 (16), 104 (23), and 91 (15). ^{1}H NMR ($CDCl_3$): δ 2.45–2.56 (3s, 3H), 4.11–4.19 (3s, 2H), 4.76 (s, ether), and 7.23–7.58 ppm (m, 9H). ^{13}C NMR: δ 19.9, 21.3, 21.6, 21.7, 39.6, 41.8, 42.1, 72.3, 126.1, 126.2, 126.2, 126.6, and 128.6 ppm.

*2.1.1.2. Benzyl alcohol with **2b**. In toluene*: A 100 mL round-bottomed flask was charged with toluene (60 mL) and a stirbar. Benzyl alcohol (0.125 g, 1.15 mmol) was added via syringe, followed by **2b** (0.75 g). A condenser with a septum with N_2 inlet and outlet needles was attached. The mixture was refluxed overnight. After cooling, the **2b** was removed by filtration through a fritted funnel and the mother liquor was analyzed by GC/MS, evaporated and analyzed by NMR to show a mixture of *o*- and *p*-benzyltoluene, along with a trace amount of benzyl ether. Evaporation of the solvent gave an oil, and purification by column (silica gel, pentane) gave *o*- and *p*-benzyltoluene (0.19 g, 91%).

*2.1.1.3. Benzyl alcohol with 33% of **2a**. In toluene*: In a 50 mL round-bottomed flask was placed a stirbar and toluene (15 mL). Benzyl alcohol (0.043 g, 0.4 mmol) was added via syringe, followed by **2a** (0.08 g) added in one portion. A condenser with a septum and N_2 inlet and outlet needles was attached and the mixture was stirred at reflux overnight. The **2a** was removed by filtration through a fritted funnel and the mixture was analyzed by GC/MS and NMR to show a mixture of *o*- and *p*-benzyltoluene and benzyl ether. No unreacted benzyl alcohol was observed.

*2.1.1.4. Benzyl alcohol with 4% **2a**. In toluene*: In a 2 L round-bottomed flask was placed toluene (750 mL) and a stirbar. Benzyl alcohol (1 mL, 9.7 mmol) was added via syringe, followed by **2a** (0.23 g) . A condenser with a septum with N_2 inlet and outlet needles was attached and the mixture was refluxed overnight. After cooling, the **2a** was removed by filtration through a fritted funnel and the mother liquor was analyzed by GC/MS, evaporated and analyzed by NMR. Spectra showed the presence of a mixture of *o*- and *p*-benzyltoluene and benzyl ether.

*2.1.1.5. Repetitive reactions of benzyl alcohol with **2a***. The **2a** recovered after each reaction was used in a subsequent reaction. This sequence was repeated for a total of five reactions with the same **2a** in toluene. A 100 mL round-bottomed flask was charged with toluene (60 mL) and a stirbar. Benzyl alcohol (0.1 mL, 1 mmol) was added via syringe, followed by **2a** (0.57 g) added in one portion. A condenser fitted with a septum with N_2 inlet and outlet needles was attached and the mixture was refluxed overnight. After cooling, the **2a** was removed by filtration through a fritted funnel and the mother liquor was analyzed by GC/MS, evaporated and analyzed by NMR. The recovered **2a** was reused *the same day*, without storing it under N_2, under the identical conditions just described for a total of five reactions. The products of each run were analyzed by GC/MS and NMR to show formation of *o*- and *p*-benzyltoluene and a small amount of dibenzyl ether. The products were isolated for the same for the first and fifth trial, and *o*- and *p*-benzyltoluene were obtained in >95 yield in all five experiments.

*2.1.1.6. Reaction of alcohols with **2a***. A 100 mL round-bottomed flask was charged with 60 mL of benzene or toluene, and a magnetic stirbar. The alcohol (about 0.1 mmol) was added, followed by **2a** (0.57 g). A reflux condenser sealed with a septum was attached, and a N_2 inlet and outlet needles were inserted in the septum. The system was stirred at reflux overnight. After cooling, the polymer was removed by filtration through a fritted funnel, and the mother liquor was analyzed by GC/MS and NMR. Where noted, evaporation of the solvent gave an oil, and the products were obtained by column chromatography.

*2.1.1.7. Diphenylmethanol [46] with **2a***. *In benzene*: Diphenylmethanol (0.18 g, 0.98 mmol) gave a dark oil (0.26 g). NMR confirmed the ratio of products. GC/MS: triphenylmethane: 244 (P^+, M^+, 100), 165 (87), 152 (19), 139 (5), and 115 (7). Bis(diphenylmethyl) ether: M^+ not observed 183 (57), 167 (P^+, 100), 152 (27), 105 (24), 77 (21). ^{1}H NMR (as a mixture) ($CDCl_3$): δ 5.31 (s, 1H), 5.46 (s, 0.5H), and 7.01–7.72 ppm (m, 21H). ^{13}C NMR: δ 56.9, 80.1, 129.0, 130.2, 127.3, 127.5, 128.4, 128.5, 128.5, 128.6, 129.6, 129.6, 142.3, and 144.0 ppm.

In toluene: Diphenylmethanol (0.18 g, 1 mmol) gave a solid (0.24 g) that GC/MS and NMR revealed to be a 47% of a mixture of *o*- and *p*-(diphenylmethyl)toluene. A trace amount (<2%) of the *m*-product was also observed. We also observed 53% of diphenylmethyl ether. Overlapping signals in the ^{1}H NMR prevented a determination of relative amounts of the isomers, and each product exhibited the same GC/MS fragmentation patterns. GC/MS: 258 (M+, P, 100%), 243 (86), 179 (29), 165 (93), 152 (13). ^{1}H NMR (as a mixture) ($CDCl_3$): δ 2.10, 2.20, 2.37 (3s, 3H), 5.40, 5.57 (2s, ^{1}H), and 6.97–7.16 ppm (m, 16H). ^{13}C NMR: δ 20.1, 21.2, 53.7, 56.7, 125.5, 125.9, 126.4, 126.5, 128.4, 128.6, 128.7, 129.2, 129.5, 129.6, 129.8, 130.6, 135.9, 136.7, 138.0, 141.087, 142.5, 143.6, and 144.3 ppm.

2.1.1.8. 1-Naphthylmethanol [47]. *In benzene*: 1-Naphthylmethanol (0.16 g, 1 mmol) gave a dark oil (0.29 g) that was analyzed by NMR and GC/MS, showing 1-phenylnaphthalene. GC/MS: 218 (P+, M+, 100), 202 (38), 189 (1), 141 (13), and 115 (14). ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 1H), 4.19 (s, 3H), and 6.96–7.79 ppm (m, 26H). ^{13}C NMR ($CDCl_3$): δ 39.2, 31.1, 36.0, 39.4, 71.0, 124.3, 124.6, 124.9, 125.3, 125.9, 126.0, 126.0, 126.1, 126.3, 126.4, 126.4, 127.0, 127.2, 127.3, 127.5, 127.6, 128.6, 128.8, 129.0, 129.1, 129.2, 129.4, 132.5, 134.1, 134.3, 135.3, 136.5, 136.9, 140.9, and 141.0 ppm. No unreacted alcohol or bis(1-naphthyl) ether were isolated.

In toluene: 1-Naphthylmethanol (0.16 g, 1 mmol) gave 0.18 g of crude material and NMR and GC/MS showed the product to be 1-(*o-, m- and p*-tolyl)naphthalene. GC/MS: 232 (P^+, M^+, 100), 217 (94), 202 (29), 141 (13), and 115 (24). ^{1}H NMR ($CDCl_3$): δ 2.34, 2.35, 2.38 (3s, 3H), 4.45, 4.46 (2s, 2H), and 7.08–8.07 ppm (m, 11H). ^{13}C NMR: δ 19.7, 21.1, 36.3, 38.7, 123.9, 124.4, 125.6, 125.6, 125.6, 125.7, 126.0, 126.0, 126.2, 126.5, 127.0, 127.1, 127.3, 128.7, 128.8, 129.2, 129.7, 130.2, 132.2, 132.3, 133.9, 134.0, 135.6, 136.2, 136.7, 136.7, 137.6, and 138.5 ppm.

2.1.1.9. Cinnamyl alcohol. *In benzene*: Cinnamyl alcohol (0.13 g, 1 mmol) gave 0.11 g of a black oil. When analyzed by NMR, only resonances in the aromatic region were observed and there were no signals we could attribute to coupling products or ether.

In toluene: Cinnamyl alcohol gives a liquid (0.14 g) and GC/MS and NMR revealed 67% of *o*- and *p*-1-phenyl-3-tolyl-1-propene, with <2% of the *meta*-product. The GC/MS data was nearly identical for each isomer, which could not be separated. GC/MS: (208 (M^+, 94), 193 (93), 115 (P^+, 100%), 104 (81), 91 (56) ^{1}H NMR ($CDCl_3$): δ 2.24, 2.27 (2s, 3H), 3.41, 3.43 (2s, 2H), 6.26–6.33 (m, 2H), and 7.01–7.27 ppm (m, 11H). ^{13}C NMR: δ 19.5, 21.1, 36.9, 39.0, 125.4, 126.0, 126.1, 126.2, 126.3, 126.5, 127.1, 127.1, 128.1, 128.3, 128.3, 128.5, 128.6, 129.1, 129.2, 129.3, 129.6, 130.3, 130.9, 130.9, 131.1, 135.7, 136.5, 137.1, 137.6, and 138.3 ppm.

2.1.1.10. 2-Buten-1-ol. *In benzene*: 2-Buten-1-ol (0.076 g, 1 mmol) gave an oil that showed <5% of 3-phenyl-1-butene, but the alcohol had been consumed. GC/MS: 132 (M^+, 53), 117 (P^+, 100), 91 (45), 103 (5), 65 (16). ^{1}H NMR ($CDCl_3$): δ 1.72–1.74 (d, 3H), 3.50–3.37 (d, 2H), 5.49–5.69 (m, 2H), and 7.19–7.35 ppm (m, 4H). ^{13}C: δ 17.9, 39.1, 125.9, 126.4, 128.351, 128.5, 130.1, and 141.1 ppm. The bromine solution did not show the presence of brominated products.

In toluene: 2-Buten-1-ol (0.09 mL, 1 mmol) gave a dark brown oil with a solid (0.15 g). GC/MS and NMR analysis showed a near quantitative yield of *o*- and *p*-3-tolyl-1-butene. GC/MS: several peaks with the same fragmentation pattern 146 (M^+, 56), 131 (P^+, 100%), 115 (21), 105 (13), and 91 (38). ^1H NMR: δ 1.71–1.77 (m, 3H), 2.33–2.37 (2d, 3H), 3.32–3.42 (m, 2H), 5.49–5.63 (2H, m), and 7.10–7.26 ppm (4H, m). ^{13}C NMR: δ 17.9, 19.3, 19.5, 21.0, 31.042, 36.5, 36.7, 126.0, 126.1, 126.1, 126.2, 128.2, 128.4, 128.6, 129.0, 129.1, 129.1, 129.2, 130.1, 130.4, 135.3, 136.2, 138.0, and 139.2 ppm.

2.1.1.11. 3-Buten-2-ol. In benzene: 3-Buten-2-ol (0.076 g, 1 mmol) gave an oil that showed 3-phenyl-1-butene was formed in <5%, identical to the products observed with 2-buten-1-ol in benzene. GC/MS: 132 (M^+, 53), 117 (P^+, 100), 91 (45), 103 (5), and 65 (16). ^1H NMR ($CDCl_3$): δ 1.71–1.75 (m, 3H), 3.34–3.36 (d, ^1H), 5.56–5.61 (m, 2H), and 7.19–7.34 ppm (m, 4H). ^{13}C NMR: δ 17.9, 39.1, 125.9, 126.4, 128.3, 128.4, 128.5, 130.1, and 141.1 ppm. The bromine solution did not show the presence of brominated products.

In toluene: 3-Buten-2-ol (0.09 mL, 1 mmol) gave an oil that showed *o*- and *p*-3-tolyl-1-butene were formed in <5%. GC/MS gave identical results as observed in the reaction of 2-buten-1-ol. GC/MS: 146 (M^+, 55), 131 (P^+, 100), 115 (21), 105 (13), and 91 (41).

2.1.1.12. 3-Methyl-2-buten-1-ol. In benzene: 3-Methyl-2-buten-1-ol (0.08 g, 1 mmol) gave an oil that showed the Friedel–Crafts products were formed in <5%. GC/MS: 146 (M^+, 51), 131 (P^+, 100), 115 (14), and 91 (63). Evaporation of the solvent revealed trace amounts of a mixture whose components could not be identified.

In toluene: 3-Methyl-2-buten-1-ol (0.093 g, 1 mmol) gave an oil (0.18 g), and analysis of the mixture showed the presence of <5% of 3-methyl-1-tolyl-2-butene, along with unidentifiable components. GC/MS: major: 160 (M^+, 50), 145 (P^+, 100), 130 (21), 105 (30), and 91 (20); minor: 160(M^+, 25), 145(5), 105(P^+, 100), 79 (9), 77 (14). ^1H NMR ($CDCl_3$): δ 1.8–1.82 (m, 5H), 2.37–2.43 (m, 4H), 3.38–3.99 (d, 2H), 5.31 (m, 1H), and 7.16–7.21 ppm (m, 4H). ^{13}C NMR: δ 17.9, 17.9, 19.5, 21.1, 25.8, 32.3, 34.0, 122.7, 123.6, 125.4, 125.9, 126.0, 128.1, 128.2, 128.3, 128.7, 128.8, 129.1, 130.1, 132.2, 132.4, 135.2, 136.2, 138.8, and 139.4 ppm.

2.1.1.13. Cyclohexanol. In benzene: Cyclohexanol (0.1 mL, 1 mmol) gave an oil that was treated with 1.0 equiv of bromine (0.05 mL, 1 mmol) and the resulting solution stirred for 20 h in the dark. At this time, the mixture was treated with 0.1 M Na_2SO_3, the organic layer separated and washed with water (3 × 20 mL) and brine, dried over magnesium sulfate and filtered. Analysis of the mixture by GC/MS and NMR showed the formation of 1,2-dibromocyclohexane, along with trace amounts of phenylcyclohexane and cyclohexanol. GC/MS: for cyclohexanol: 100 (M^+, 2), 82 (45), 67 (28), and 57 (P^+, 100). For 1,2-dibromocyclohexane: 240/242/244 (M^+, 9/16/8) 161/163(17/16), and 81 (P^+, 100).

In toluene: Cyclohexanol (0.1 mL, 1 mmol) gave an oil that was treated with 1.0 equiv of bromine (0.05 mL, 1 mmol), and the solution stirred for 20 h in the dark. The reaction mixture was treated with 0.1 M Na_2SO_3, the organic layer separated and washed with water (3 × 20 mL) and brine, dried over magnesium sulfate and filtered. Analysis of the mixture by GC/MS and NMR showed the formation of 1,2-dibromocyclohexane along with trace amounts of tolylcyclohexane. GC/MS: for 1,2-dibromocyclohexane: 240/242/244 (M^+, 9/16/8) 161/163 (17/16), and 81 (P^+, 100).

2.1.1.14. 1-Octanol. In benzene: 1-Octanol (0.16 mL, 1 mmol) gave an oil that showed the presence of unreacted alcohol along with octenes, but the octenes were not confirmed by NMR.

In toluene: 1-Octanol (0.16 mL, 1 mmol) gave an oil that showed unreacted alcohol, but no indication of octenes. An oil was recovered after evaporation (0.22 g).

2.1.1.15. 2-Octanol. In benzene: 2-Octanol (0.16 mL, 1 mmol) gave an oil that showed a mixture of unreacted starting material and unidentified compounds were observed.

In toluene: 2-Octanol (0.16 mL, 1 mmol) gave an oil that showed unreacted starting material and trace amounts of ether and hydrocarbons.

2.1.1.16. Benzyl alcohol with 1.0 equiv of triflic acid. A 100 mL round-bottomed flask was charged with a stirbar and benzene (60 mL). Benzyl alcohol (0.12 mL, 1.13 mmol) was added via syringe, followed by triflic acid (0.1 mL, 1.13 mmol), added via syringe in one portion. A condenser with a septum with N_2 inlet and outlet needles was attached and the mixture was refluxed overnight. After cooling, the mixture was washed with saturated sodium bicarbonate (3 × 20 mL), water (3 × 20 mL) and brine. The organic layer was dried with magnesium sulfate, filtered and evaporated to give 0.28 g of an oil, which NMR and GC/MS showed to be a mixture of diphenylmethane and a mixture of *o*- and *p*-dibenzylbenzene. No unreacted benzyl alcohol remained. GC/MS: for diphenylmethane: 168 (M^+, 93), 167 (P, 100%), 152 (23), 91 (19), 65 (13), and 51 (13). For dibenzylbenzene #1: 258 (M^+, 43), 167 (P^+, 100), 152 (17), 178(5), and 91 (12). For dibenzylbenzene #2: 258(M^+, 50), 179 (P^+, 100), 165 (61), 152 (19), and 91 (11). ^1H NMR ($CDCl_3$) (as a mixture): δ 4.10, 4.15 (2s, 2H), and 7.27–7.47 ppm (m, 10H). ^{13}C NMR: δ 42.1, 126.3, 128.6, 129.1, and 141.3 ppm.

2.1.1.17. Benzyl alcohol with 33% triflic acid. A 100 mL round-bottomed flask was charged with benzene (60 mL) and a magnetic stirbar. Benzyl alcohol (0.35 mL, 3.4 mmol) was added via syringe, followed by triflic acid (0.1 mL, 1.13 mmol) added via syringe. A condenser with a septum with N_2 inlet and outlet needles was attached and the mixture was refluxed overnight. After cooling, the mixture was washed with saturated sodium bicarbonate (3 × 20 mL), water (3 × 20 mL) and brine. The organic layer was dried over magnesium sulfate, filtered and evaporated to give 0.78 g of the liquid. Spectral analysis (GC/MS and NMR) showed primarily diphenylmethane with only a trace amount of dibenzylbenzene. No unreacted alcohol was observed.

2.1.1.18. Benzyl alcohol with 5% triflic acid. A 100 mL round-bottomed flask was charged with benzene (60 mL) and a magnetic stirbar. Benzyl alcohol (2.3 mL, 22 mmol) was added via syringe, followed by triflic acid (0.1 mL, 1.13 mmol) added via syringe. A reflux condenser equipped with a septum with N_2 inlet and outlet needles was attached. The mixture was stirred at reflux overnight, cooled and then washed with saturated sodium bicarbonate (3 × 20 mL), water (3 × 20 mL) and brine. The organic layer was then dried over magnesium sulfate, filtered and evaporated to give 2.74 g of crude mixture of several products. All of the benzyl alcohol was consumed. Analysis showed approximately a 2:1 mixture of diphenylmethane:dibenzylbenzene.

2.1.1.19. Benzyl alcohol with 1.0 equiv of triflimide. A 100 mL round-bottomed flask was charged with a stirbar and toluene (60 mL). Benzyl alcohol (0.11 mL, 1 mmol) was added via syringe, followed by bis(trifluoromethanesulfonamide) (0.28 g, 1 mmol), in one portion. A condenser with a septum with N_2 inlet and outlet needles was attached and the mixture was refluxed overnight. After cooling, the mixture was washed with saturated sodium bicarbonate (3 × 20 mL), water (3 × 20 mL) and brine. The organic layer was dried with magnesium sulfate, filtered and evaporated to give 0.39 g of a black oil, which NMR and GC/MS showed to be a mixture of *o*- and *p*-dibenzyltoluene (about 95%). No unreacted benzyl alcohol remained.

2.1.1.20. Benzyl alcohol with 1.0 equiv of lithium triflate. Lithium triflate (0.16 g, 1 mmol) was added to a 100 mL round-bottomed flask containing a solution of benzyl alcohol (0.11 mL, 1 mmol) in toluene (60 mL) and a magnetic stirbar. A condenser with a septum and N_2 inlet and outlet needles was attached and the mixture stirred at reflux overnight. The mixture was filtered and the solvent evaporated to give an oil (0.13 g). Spectral analysis (NMR and GC/MS) revealed only benzyl alcohol and small amounts of toluene. No benzyltoluene or dibenzyl ether was observed.

Acknowledgment

We thank Dr. Martha Morton, coordinator of the NMR facility, and Mr. Marvin Thompson, coordinator of the mass spectrometer facility, for their generous help in this work. Dr. Gregory A. Sotzing thanks NSF (CAREER − CHE 0349121) for the financial support of this work.

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[46] Benzophenone (3 g, 16.5 mmol) was dissolved with stirring in fresh absolute ethanol (200 mL). The system was immersed in an ice bath and NaBH$_4$ (1.21 g, 31.88 mmol) was then added. After ~20 h, 1.5 g of additional NaBH$_4$ was added, and after 59 total hours, saturated ammonium chloride (50 mL) was added slowly. The solvents were evaporated and the residue was taken up in water (50 mL, and extracted with ethyl acetate (3 × 100 mL). The organic phases were combined, washed with brine and dried over MgSO$_4$, filtered and evaporated to give pure diphenylmethanol as a white solid (2.55 g, 84%). GC/MS: 184(M$^+$, 45), 165 (14), 105 (P$^+$, 100), 77 (60), 51 (28). ^{1}H NMR (CDCl$_3$) δ: 2.51 (bs, 1H), 5.88, 6.48 (2s, 1H), 7.27–7.48 (m, 10H). ^{13}C NMR: δ 76.3, 77.3, 126.5, 126.7, 127.2, 127.6, 128.4, 128.6, 143.8, 143.9.

[47] This alcohol was prepared by reduction with sodium borohydride as follows: 1-Naphthaldehyde (10 g, 64 mmol) was loaded into a 300 mL round-bottomed flask with a stir bar and fresh, absolute ethanol (150 mL). Then, NaBH$_4$ (4.84 g, 128 mmol) was added at 0 °C and the reaction stirred for about 50 h while warming to ambient temperature. The reaction was cooled with ice and saturated ammonium chloride (100 mL) was added. Evaporation of ethanol was followed by extraction with CH$_2$Cl$_2$ (3 × 60 mL). The combined organic phases were washed with brine, dried over MgSO$_4$, filtered and evaporated to give a yellow oil, that on standing, gave a solid. Recrystallization from petroleum ether gave an off-white solid (8.6 g, 85%). GC/MS: 158 (M$^+$, 45), 141 (11), 129 (P$^+$, 100), 115 (13). ^{1}H NMR (CDCl$_3$) δ: 1.90 (bs, 1H), 5.17 (s, 2H), 7.45–7.59 (m, 4H), 7.83–7.93 (m, 2H), 8.14–8.17 (dd, 1H). ^{13}C NMR: δ 63.7, 123.7, 125.4, 125.4, 125.9, 126.4, 128.6, 128.79, 131.3, 138.8, 136.3.